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Effect of traps on the performance of bulk heterojunction organic solar cells

M. M. Mandoc
Zernike Institute for Advanced Materials and Dutch Polymer Institute, University of Groningen, Nijenborgh 4, NL-9747AG Groningen, The Netherlands

F. B. Kooistra, J. C. Hummelen, B. de Boer, and P. W. M. Blom[a)]
Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, NL-9747AG Groningen, The Netherlands

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The effect of electron traps on the performance of bulk heterojunction organic solar cells made of poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] blended with [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) is investigated. By deliberately introducing 7,7,8,8-tetracyanoquinodimethane, which is a stronger electron accepting molecule than PCBM, the electron transport in the solar cells becomes trap limited. We demonstrate that the open circuit voltage and its light-intensity dependence are strongly affected by recombination of holes with trapped electrons. Depending on the amount of traps, their recombination strength, and the light intensity, the losses due to trap-assisted recombination can even dominate over the intrinsic bimolecular recombination. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2821368]

Organic solar cells have been intensively studied over the last years for their potential in obtaining clean energy at low costs. They are lightweight, flexible, and easy to produce. With bulk heterojunctions (BHJ) of conjugated polymers and methanofullerenes, efficiencies of 2.5% have been obtained for blends based on poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene] (MDMO-PPV) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM).[1] Furthermore, efficiencies reaching up to 4% have been obtained for slowly dried blends of poly(3-hexylthiophene) and PCBM.[2–4] In these polymer-fullerene BHJ solar cells the electron transfer from the donor to the acceptor leads to a Coulombically bound electron-hole pair, which still needs to dissociate into free carriers.[5] The competing mechanism is the bimolecular Langevin recombination, in which free carriers recombine to revive the bound pair. The bound pair is metastable and during its lifetime it can undergo multiple dissociations with subsequent carrier recombination.[6] Furthermore, it has been demonstrated that the open-circuit voltage V_{oc} of BHJ solar cells, with trap-free electron and hole transport and bimolecular recombination as the only loss mechanism, scales with the light intensity with a slope S of (kT/q).[7] This dependence has been experimentally verified for MDMO-PPV:PCBM solar cells.[7]

From the absorption point of view, it is attractive to use conjugated polymers also as acceptors. A major problem to use conjugated polymers of PPV as acceptors in BHJ solar cells is that their electron transport is often trap-limited.[8] Also for cyano-PPV derivatives that are used as acceptors in all-polymer solar cells, the electron transport is trap limited, also in the blend.[9] It is not clear yet what the nature of these traps is and what would be the way of producing electron trap-free PPV derivatives. Furthermore, all-polymer solar cells show an anomalously strong dependence of V_{oc} on the light intensity.[10] This has been explained by the fact that free holes in the donor can also recombine with trapped electrons in the acceptor. This process does not occur in their PCBM counterpart, a material which shows trap-free electron transport as well as a free electron mobility[11] μ_n of $\sim 10^{-7}$ m^2/V s, which is higher than for acceptor PPV derivatives with μ_n of only $10^{-11}-10^{-10}$ m^2/V s.[9,12] In order to verify the effects of electron traps on solar cell performance we deliberately introduce electron traps in MDMO-PPV:PCBM based blends. We show that the operation characteristics of these trap-limited solar cells are similar to the all-polymer cells, where the traps are intrinsically contained in the acceptor polymer itself.

In solar cells with both trap-free electron and hole transport in the acceptor and donor, respectively, the main recombination mechanism for the free charge carriers is bimolecular recombination. The bimolecular recombination rate is given in this case by

$$R = \gamma(np - n_i p_i), \tag{1}$$

where n (p) is the free electron (hole) density, n_i (p_i) is the intrinsic electron (hole) density, and γ is the Langevin recombination constant. In case of a pristine material, the recombination constant is governed by the sum of electron and hole mobility[13]

$$\gamma = \frac{q}{\varepsilon}(\mu_n + \mu_p), \tag{2}$$

with q the elementary charge, ε the dielectric constant, and $\mu_{n(p)}$ the electron (hole) mobility. However, in case of a blend, the slowest carrier dominates the recombination, as the fastest one cannot cross the interface between the two materials, and must wait for the slowest carrier in order to recombine.[14] In this case, the recombination constant is given by[14]

$$\gamma = \frac{q}{\varepsilon}\min(\mu_n, \mu_p). \tag{3}$$

[a)]Electronic mail: p.w.m.blom@rug.nl.

When electron traps are present in the acceptor, the dissociation of the bound pairs at the interface leads again to free carriers, but now part of the electrons will be trapped. For the electrons trapped close to the interface there is a probability to recombine with the free holes, leading to the loss of both carriers. The trap-assisted recombination rate is given by the Shockley-Read-Hall (SRH) equation[15,16]

$$R = C_n C_p N_t (pn - p_1 n_1)/[C_n(n+n_1) + C_p(p+p_1)], \qquad (4)$$

where C_n and C_p are the capture coefficients of electrons and holes, respectively, N_t is the density of electron traps, n and p are the electron density in the conduction band and the hole density in valence band, and $p_1 n_1 = N_c N_v \exp[-(E_c - E_v)/kT] = n_i^2$, with n_i the intrinsic carrier concentration in the sample. This trap-assisted process adds to the Langevin recombination, contributing to the loss mechanisms in a BHJ organic solar cell. We note that the escape probabilities from the traps for both electrons and holes are taken into account in the SRH equation.

For PCBM, which is a trap-free material with a lowest unoccupied molecular orbital (LUMO) at 3.7 eV,[17] a stronger electron accepting molecule must be used as an electron trap. One such molecule is 7,7,8,8-tetracyanoquinodimethane (TCNQ), with a LUMO at 4.5 eV,[18] known from the charge transfer salts formed by its radical anion $(TCNQ)^-$.[19,20] In photovoltaics and light emitting diodes, TCNQ and its derivatives have been used as dopant, leading to an increase in the hole mobility or to the lowering of injection barriers.[18,21–23] Furthermore, it has been shown that there is an electron transfer from conjugated polymers to TCNQ and its derivatives, the efficiency of this process being in some cases correlated to the acceptor strength of the molecules.[24]

The solar cells were fabricated on indium-tin oxide coated glasses on which poly(3,4-ethylenedioxythiophene):polystyrenesulphonate was spin coated. Subsequently, the blend active layer was spin coated from a chlorobenzene solution, under a nitrogen atmosphere. As a top electrode, 1 nm of lithium fluoride (LiF) followed by 100 nm of aluminum was deposited at a chamber pressure of $\sim 10^{-6}$ mbar. The devices were characterized in a nitrogen atmosphere, using a Steuernagel SolarConstant 1200 light source with the highest intensity at 1200 W/m^2 and the intensity dependence of the V_{oc} was measured using a set of neutral filters. The standard solar cells were prepared using a 1:4 weight ratio MDMO-PPV:PCBM blend. PCBM was synthesized at the University of Groningen. TCNQ (Sigma Aldrich) was used as provided. For the trap-limited cells, the same PPV:PCBM weight ratio was used as for standard cells, with 1% of the PCBM molecules being replaced by TCNQ.

The addition of TCNQ to the PPV:PCBM blend clearly lowers the performance of the solar cells. As shown in Fig. 1, the addition of TCNQ results in a lower current and a lower V_{oc}. The power conversion efficiency decreases from $\sim 2.0\%$ in case of the standard MDMO-PPV:PCBM cells to $\sim 0.6\%$ for the trap-limited MDMO-PPV:PCBM:TCNQ cells. There is also a decrease in the fill factor, from $\sim 52\%$ for the standard devices to $\sim 42\%$ for the trap-limited case.

In case of Langevin recombination being the only loss mechanism, it has been shown that the open circuit voltage V_{oc} of the solar cells is given by[7]

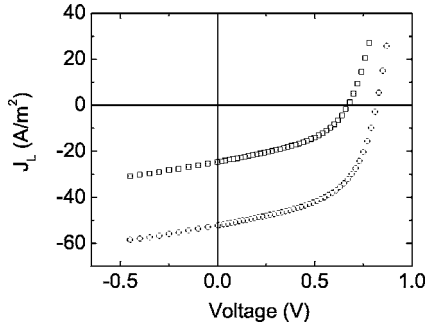

FIG. 1. Photocurrent J_L-V characteristics under illumination of a standard MDMO-PPV:PCBM solar cell (circles) and of a trap-limited MDMO:PPV:PCBM:TCNQ solar cell (squares). In both cases, the thickness of the active layer is 90 nm.

$$V_{oc} = \frac{E_{gap}}{q} - \frac{kT}{q} \ln\left[\frac{(1-P)\gamma N_c^2}{PG}\right], \qquad (5)$$

where E_{gap} is the energy difference between the highest occupied molecular orbital (HOMO) of the electron donor and the LUMO of the electron acceptor, q is the elementary charge, k the Boltzmann constant, T the temperature, P is the dissociation probability of the electron-hole pairs into free carriers, γ the recombination constant, N_c the density of states in the conduction band, and G the generation rate of electron-hole pairs. This formula contains the dependence of the V_{oc} on the light intensity, as G is the only term directly proportional with the light intensity (with P and γ not depending on it). Therefore, the formula predicts the slope $S = (kT/q)$ of the V_{oc} versus the natural logarithm of the light intensity, as has been verified for MDMO-PPV:PCBM solar cells.[7]

For all-polymer solar cells, however, with electron traps intrinsically contained in the acceptor phase, a slope of 1.5 (kT/q) has been measured.[10] We have explained this deviation from Eq. (5) by including trap-assisted recombination in the recently developed device model for BHJ solar cells.[25] The trap-assisted recombination competes with the Langevin one, thereby enhancing the dependence of the V_{oc} on the light intensity. The value of the slope of V_{oc} versus natural logarithm of the light intensity depends on the strength of the recombination.[10] In Fig. 2, the dependence of V_{oc} on the light

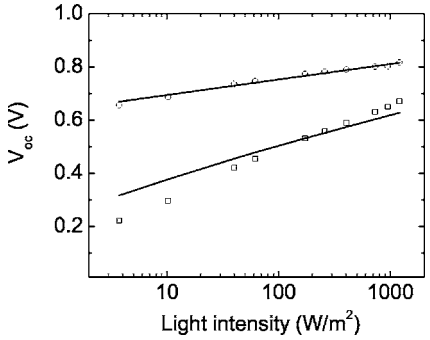

FIG. 2. Experimental V_{oc} light intensity dependence for a trap-free MDMO-PPV:PCBM solar cell (circles) and in case of trap-limited MDMO-PPV:PCBM:TCNQ cell (squares). The solid lines are the calculated values of the V_{oc}, corresponding to the two cases, with $\mu_n = 2.0 \times 10^{-7}$ m^2/V s, $\mu_p = 2.0 \times 10^{-8}$ m^2/V s, and a relative dielectric constant $\varepsilon_r = 3.4$. In case of trapping, a density $N_t = 7.93 \times 10^{24}$ m^{-3}, with a single level depth $E_t = 0.6$ eV has been assumed, and a capture rate given by $C_n = C_p = 1.0 \times 10^{-15}$ m^3 s^{-1}.

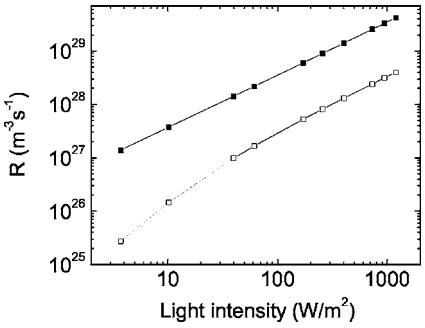

FIG. 3. Rate of Langevin recombination (open symbols) and of trap-assisted recombination (closed symbols) as function of light intensity, corresponding to the calculated V_{oc} values of the trap-limited solar cell from Fig. 2.

intensity is shown for a MDMO-PPV:PCBM trap-free solar cell, with $S=1.05$ (kT/q) (calculated from the linear fit) and for a trap-limited MDMO-PPV:PCBM:TCNQ one, with $S=3.04$ (kT/q). This dependence is stronger as observed for the all-polymer cells, where for the acceptor polymers an exponential distribution of traps in energy has been found, with a density less than 10^{23} m^{-3}. In the MDMO-PPV:PCBM:TCNQ case, with all identical TCNQ molecules as traps, as a first approximation a single trapping level would be more likely, not a distribution. Since the TCNQ trap density is $N_t=7.93\times10^{24}$ m^{-3}, being two orders of magnitude higher than the trap density in the acceptor polymers, it is expected that the trap-limited recombination is stronger. As a result also the dependence of V_{oc} is more enhanced. The lines in Fig. 2 are calculated using the BHJ device model for a trap-free cell, and for the trap-limited case with single level traps of density $N_t=7.93\times10^{24}$ m^{-3}, situated at $E_t=0.6$ eV with respect to the transport sites. The capture coefficients for electrons and holes $C_n=C_p=1.0\times10^{-15}$ m^3 s^{-1}. In the calculations, the dielectric constant of the blend and the mobility values for electrons and for holes, derived from charge transport measurements have been used.[11,26] The decay of the V_{oc} for the trap-limited solar cells is a direct result of the fact that the presence of electrons in trap levels below the LUMO of the PCBM leads to a lowering of the electron quasi-Fermi level. It should be noted that the TCNQ molecules can also be present in the MDMO-PPV phase, where they can act as exciton dissociation site and/or electron trap. In the solar cell this would mean that the amount of excitons reaching the donor-acceptor interface would be reduced. In our model this would translate as a different value for G. We verified that a decrease of G by a factor of 2 does not change the dependence of V_{oc} on the natural logarithm of light intensity or the values found for C_n and C_p.

For such a strong dependence of V_{oc} on the light intensity it is expected that the trap-assisted recombination dominates over the Langevin recombination. As it can be seen in Fig. 3, this is true at all light intensities measured. With increasing light intensity, leading to an enhanced carrier density in the device, the Langevin recombination becomes quadratically stronger ($\sim np$) and eventually will take over the trap-assisted recombination [$\sim n(p)$]. Therefore, it is expected that at higher light intensities the slopes in Fig. 3 will change, with a crossover point marking the new regime where Langevin recombination is dominant.

The increased amount of recombination in the trap-limited solar cells also leads to a reduction of the fill factor.[14] Furthermore, the additional loss of free charge carriers due to the trap-limited recombination leads to a reduction of the photocurrent. The combination of these effects then leads to a lowering of the solar cell performance of typically a factor of 3–4 for the amount of traps used in this study.

In conclusion, the introduction of TCNQ electron traps in blends of MDMO-PPV:PCBM clearly modifies the open circuit voltage and its dependence on light intensity. The main signature of trap-assisted recombination is the enhanced dependence of the open circuit voltage on the light intensity, with a slope $S>(kT/q)$. The trap-assisted recombination can dominate over the Langevin recombination. The enhanced recombination losses also lower the fill factor and short circuit current. The design of materials without deep traps is therefore an essential condition for future efficient organic solar cells.

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